Detrimental Ni(0) transfer in Kumada catalyst transfer polycondensation of benzo[2,1-*b*:3,4-*b*']dithiophene

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ABSTRACT

This paper deals with the Kumada Catalyst Transfer Polycondensation (KCTP) of 4,7-dioctylbenzo[2,1-*b*:3,4-*b*']dithiophene (**BDP-Oct**) using Ni(II) catalyst or In/cat combination. A combination of MALDI MS, GPC and ^{31}P NMR spectroscopy is used to reveal the failure of the KCTP of this particular monomer. Intermolecular transfer reactions to monomer appeared to prevent the formation of polymer. This result is remarkable, since isomeric benzo[1,2-*b*:4,5-*b*']dithiophene polymerizes in a controlled way. The presence of a "non-aromatic double bond" in annulated monomers is discussed.

KEYWORDS: Living polymerization, conducting polymers, MALDI, metal-polymer complexes, KCTP

INTRODUCTION

In the past couple of decades, conjugated polymers (CPs) having fused aromatic rings has been an important topic of research due to their interesting optoelectronic properties and ability to furnish a variety of materials in organic electronics. In this respect, 4,8-disubstituted benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) (Fig. 1) is a superior candidate over many others when applied in polymer solar cell and field effect transistors. This can be attributed to the large planar conjugated structure of the BDT unit, so that polymers can easily form π-π interactions.[1-4] Another fused building block, cyclopenta[2,1-*b*;3,4-*b*']dithiophene (CPDT)[5], that consists of a thiophene dimer bridged in the 3,3'-position by a saturated carbon atom, has shown its potential in materials for organic electronics.[6,7]

A major change in the synthesis of the CPs (from the reported and vastly used conventional step growth polymerization) occurred when the research groups of Yokozawa and McCullough developed their controlled chain growth polymerization in 2004.[8,9] They used Ni(dppp)Cl_2 catalyst (dppp= 1,3-bis(diphenylphosphino)propane) in combination with organomagnesium or zinc monomers of 3-hexylthiophene. This protocol leads to low dispersities, high molar mass polymers and allows preparing fully conjugated block copolymers and other supramolecular structures in one-pot polymerizations.[10,11] This procedure enables the controlled synthesis of poly(3-alkylthiophene)s, poly(3-alkylselenophene)s,[12,13] poly(phenylene)s,[14] poly(pyridine)s,[15] poly(pyrrole)s,[16] poly(bithienylmethylene)s[17], poly(dithieno[3,2-b; 2',3'-d]- silole)s,[18] poly(fluorene)s,[19] poly-(cyclopenta[2.1-*b*:3,4-*b'*] dithiophene)[20] and many block copolymers[21]. Such a broad

diversity in the targeted monomers clearly reveals the increasing interest in developing controlled polymerization procedures of CPs, using methods such as the Kumada catalyst transfer polycondensation (KCTP).

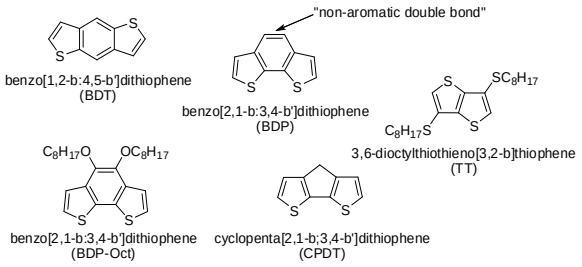


FIGURE 1 Structure of various isomers of benzodithiophene, TT and CPDT.

The main requirement to steer these organometallic polycondensations into the "living" polymerization is to find suitable conditions for the formation of an associative π-complex[22,10] between the growing polymer and the catalytic species generated after the reductive elimination. In this respect, three possible side-reactions can hamper the controlled synthesis of CPs. First, the interaction between the growing polymer the catalyst can be too weak, resulting in the diffusion of the catalyst. This is the reason why electron deficient monomers are notoriously difficult to polymerize in a controlled way.[23] Second, the monomer can also interact with the catalyst of the "associative pair" resulting in a transfer reaction. This was observed by Nojima *et al*[24] in the case of a monomer containing a double bond. Third, recently, we observed that the KCTP of 3,6-dioctylthiothieno [3,2-*b*]thiophene (TT) is not possible due to a very strong association of the catalyst with the "non-aromatic double bond" – a double bond that is not necessary to have an aromatic structure- in TT, poisoning the catalyst.[25] The peculiar feature of TT is that the difference in energy of the whole TT cycle and thiophene in conjugation with the additional double bond is only very small. Interaction of this catalyst with the "double bond" requires only a small decrease in energy, allowing a strong interaction. This suggests that the polymerization of annulated rings bearing such a "non-aromatic double bond" is very difficult, as a very strong complexation with the catalyst can be expected.

An interesting set of annulated rings to test this hypothesis is BDT and isomeric benzo[2,1-*b*:3,4-*b*']dithiophene (BDP).[26] BDP can be considered has as an analogue of CPDT in which the non-conjugated sp^2 C-atoms would be involved into the "non-aromatic double bond". Similarly to BDT, BDP presents electron rich (thiophene) rings, with BDT lacking the "non-aromatic double bond". While a BDT-based monomer was polymerized in chain-growth manner by Stefan *et al*,[27] similar polymerization of BDP has never been reported. So, we attempt here the KCTP of 4,7-dioctylbenzo[2,1-*b*:3,4-*b*']dithiophene (**BDP-Oct**) using various Ni based catalysts to investigate the effect of that "non-aromatic double bond" connecting both the thiophene rings fused at the either sides of the benzene ring.

EXPERIMENTAL

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, or Alfa Aesar. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). The dicarbonyl compound **1** was synthesised from 3-bromothiophene according to previously reported procedure.[28] Melting points were determined on a Reichert Thermovar. IR spectra were recorded from 400 to 4000 cm^{-1} on a Bruker Alpha Sample compartment RT-DL a T65 ATR platinum diamond with max resolution 2.00 cm^{-1}. *N,N'*-dimethylformamide (DMF) was double distilled over molecular sieve 4 Å. Gel permeation chromatography (GPC) measurements were done using a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in THF as eluent toward polystyrene standards with a flow rate of 1 mL/min. Electron ionization mass spectra (EI-MS) were recorded using an Agilent HP5989,

whereas the MALDI-ToF mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd-YAG laser (3rd harmonic, 355 nm) using trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix as already reported elsewhere.[29] ^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 and 600 MHz (some are processed using DELTA software from JEOL). The ^{31}P NMR chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 (δP=0.00 ppm). Always before adding the GRIM monomer to the catalyst a part of it was quenched with acidified THF in order to verify complete conversion. All attempts of polymerization in this report were always aimed to afford polymers with 20 units of **BDP-Oct**.

Synthesis of the monomers

4,5-Bis(octyloxy)benzo[2,1-b;3,4-b′]dithiophene 2

A solution of **1** (0.700 g, 3.18 mmol) in dry DMF (20 mL) was purged with argon before addition of $Na_2S_2O_4$ (0.405 g, 2.33 mmol). Then, the mixture was vigorously stirred at room temperature. After 10 min, K_2CO_3 (1.76 g, 12.8 mmol), tetrabutylammonium bromide (0.317 g, 0.98 mmol), NaI (0.195 g, 0.98 mmol), and 1-bromooctane (2.465 g, 12.76 mmol) were all added to the reaction mixture at once and stirred at 80 °C for additional 20 h. The reaction mixture was poured into excess water and the aqueous layer was extracted with dichloromethane. The combined organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The obtained crude product was purified by silica gel column chromatography affording colorless liquid **2**. Yield: 0.354 g (25%). IR (KBr): 2922, 2852, 1413, 1378, 1214, 1092, 1041, 950, 729, 660. cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.50 (d, 2H), 7.35 (d, 2H), 4.19 (m, 4H), 1.88 (q, 4H), 1.52 (m, 4H), 1.32 (br, 16H), 0.91 (t, *J* = 6.81 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 143.3, 134.2, 129.1, 124.0, 121.9, 74.3, 31.8, 29.4, 29.3, 26.1, 22.6, 14.1. MS (EI, m/z): $[M]^+$ calcd. for $C_{26}H_{38}O_2S_2$ 446.2, found 446.2.

2,7-Dibromo-4,5-bis(octyloxy)benzo[2,1-b;3,4-b′]dithiophene 3

0.659 g (0.450 mmol) of **BDP-Oct 2** was dissolved in 10 mL of a 1:1 mixture chloroform and acetic acid. *N*-bromosuccinimide (NBS) (176 mg, 0.98 mmol) was added to the previously stirred solution of **2** at 0 °C in two portions under dark. The mixture was then stirred at room temperature for three additional hours. The solvents were evaporated and the residue was loaded on short silica gel column and eluted with hexane to get 0.830 g of pure **3** as a liquid that becomes waxy solid on standing. Mp = 36 °C. IR (KBr): 2953, 2918, 2878, 2848, 1469, 1421, 1378, 1277, 1209, 1167, 1066, 940, 830, 812, 780 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.44 (s, 2H), 4.14 (t, *J* = 6.69 Hz, 4H), 1.84 (t, *J* = 6.99 Hz, 4H), 1.52 (m, 4H), 1.33 (br, 16H), 0.91 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 142.7, 134.1, 128.9, 124.6, 112.7, 74.3, 74.3, 31.8, 30.3, 29.4, 29.2, 26.0, 22.6, 14.1. MS (EI, m/z): $[M]^+$ calcd. for $C_{26}H_{36}Br_2O_2S_2$ 604.0, found 604.1.

2-Bromo-4,5-bis(octyloxy)benzo[2,1-b;3,4-b′]dithiophene 6

Method 1: NBS (0.192 g, 1.08 mmol) was added in five portions with regular intervals of 6 h to a solution of **2** (0.482 g, 1.08 mmol) in 10 mL of a THF kept at 0 °C under dark and then stirred under rt for 3 h. Water was added to the solution and the aqueous layer was extracted with dichloromethane. The organic layers were mixed, dried over $MgSO_4$ and concentrated to get crude light yellow liquid. A long silica gel column chromatography using hexane as eluent afforded 0.276 g of pure semi solid mass **6** from the crude. Yield: 50%.

Method 2: The same reaction was performed in presence of 2-3 drops of HCl and adding NBS in three portions with regular intervals of 1 h. The reaction finished within 3 h followed by same work up and purification methods as above to receive 0.4 g of 6. Yield = 70%. IR (KBr): 2922, 2852, 1461, 1417, 1374, 1355, 1310, 1285, 1238, 1190, 1091, 1045, 961, 946, 826 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.48 (s, 1H), 7.46 (s, 1H), 4.17 (m, 4H), 1.86 (m, 4H), 1.51 (m, 4H), 1.33 (br,

16H), 0.91 (m, 6H). ^{13}C NMR ($CDCl_3$, δ): 143.6, 142.4, 134.4, 133.9, 129.9, 128.2, 124.7, 124.4, 121.9, 112.3, 74.3, 31.8, 30.38, 30.36, 29.4, 29.2, 26.14, 26.11, 22.6, 14.1. . MS (EI, m/z): $[M]^+$ calcd. for $C_{26}H_{37}BrO_2S_2$ 526.1, found 526.2.

2-Bromo,7-iodo-4,5-bis(octyloxy)benzo[1,2-b:6,5-b′]dithiophene 7

Iodine (0.438 g, 1.73 mmol) and iodobenzene diacetate (0.724 g, 2.24 mmol) were added successively to a stirred solution of **6** (1.82 g, 3.453 mmol) in 20 mL of dichloromethane at 0 °C, and the mixture was stirred at room temperature for 6 h. Then, 10% aqueous $Na_2S_2O_3$ was added for washing any excess iodine, and the mixture was extracted with dichloromethane. The washed organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude was purified by silica gel column chromatography (eluent: hexane) to give **7** as 2.02 g of colorless solid. Yield = 90%. Mp = 54 °C. IR (KBr): 2953, 2918, 2870, 2850, 1467, 1417, 1368, 1273, 1209, 1171, 1093, 1012, 971, 820. cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.63 (s, 1H), 7.43 (s, 1H), 4.14 (m, 4H), 1.84 (m, 4H), 1.52 (m, 4H), 1.32 (br, 16H), 0.91 (m, 6H). ^{13}C NMR ($CDCl_3$, δ): 142.5, 142.3, 135.5, 134.0, 132.7, 121.7, 128.6, 124.6; 113.0; 74.9; 74.3, 31.8, 30.3, 29.4, 29.2, 26.0, 22.6, 14.1. MS (EI, m/z): $[M]^+$ calcd. for $C_{26}H_{36}BrIO_2S_2$ 650.0, found 650.0.

Kumada cross-coupling of 3-bromothiophene and *n*-butylmagnesiumchloride

*In absence of **2**:*

3-bromothiophene (0.1 mmol; 16.3 mg) and $Ni(dppp)Cl_2$ (2 mol%; 1.1 mg) were dissolved in dry Et_2O (5 mL) in a flask, kept under argon atmosphere. To this mixture, *n*-butylmagnesium chloride (60 µL; 2.00 M in THF) was charged dropwise. After 2 hours, an aliquot of the reaction was washed off the salts with distilled water and the ether layer was analyzed with ^{1}H NMR specroscopy (Fig. S12, S12) of the crude reaction mixture.

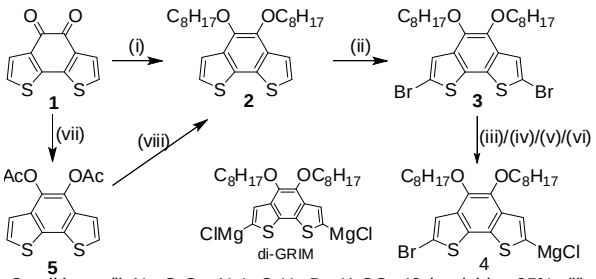
*In presence of **2**:*

3-bromothiophene (0.1 mmol; 16.3 mg) was mixed to a previously stirred solution of **2** (5 mol%, 3.0 mg) and $Ni(dppp)Cl_2$ (2 mol%; 1.1 mg) in dry Et_2O (5 mL) in a flask, kept under argon atmosphere. To this mixture, *n*-butylmagnesium chloride (60 µL; 2.00 M in THF) was charged dropwise. After 2 hours, an aliquot of the reaction was washed off the salts with distilled water and the ether layer was analyzed with ^{1}H NMR spectroscopy (Fig. S13, S13) of the crude reaction mixture.

RESULTS AND DISCUSSION

Synthesis of the monomers

In order to prepare poly(4,7-dioctylbenzo[2,1-b:3,4-b']dithiophene) (**PBDP-Oct**), two methods have been undertaken. According to a previously reported procedure,[28] the dicarbonyl compound **1** was obtained from 3-bromothiophene. In a first way (Scheme 1), **1** was subjected to consecutive acetylation (vii) and alkylation (viii) reactions to afford **2** in an overall yield of 83%. As an alternative route, **2** was synthesized in one step from compound **1** simply by reduction with sodium dithionite in dry dimethylformamide (i) and quenching the *in situ* formed dianion with bromooctane under inert atmosphere with a yield of 25% (scheme 1). Next, **2** was symmetrically brominated using a little more than two equivalents of NBS in chloroform/acetic acid mixture. Given the requirement of extreme purity for the Grignard metathesis (GRIM) polymerization (Scheme 1), the dibromo derivative **3** was further purified by silica column using hexane as the eluent.



Conditions: (i) $Na_2S_2O_4$, NaI, $C_8H_{17}Br$, K_2CO_3,48 h, yield = 25%; (ii) NBS (2.2 eq), $CHCl_3$/AcOH (1:1), 0°C to rt, 4 h, yield = 93% Reaction of **3** with ^{i}PrMgCl in THF (iii) 0.5 h, yield[a] = 50%; (iv) 1 h, yield[a] = 75%; (v) 24 h, yield[a] = 75% and (vi) 1-4 h at 0°C, Yield = 50%. [a] NMR yield. The other reported route to **2** involves (vii) Zn dust, Ac_2O, Et_3N, CH_2Cl_2, overnight and (viii) 1-bromooctane, Cs_2CO_3, ACN, reflux, 72 h with overall yield of 83%.

SCHEME 1 Synthetic strategy to dibromo precursor monomer and actual monomer.

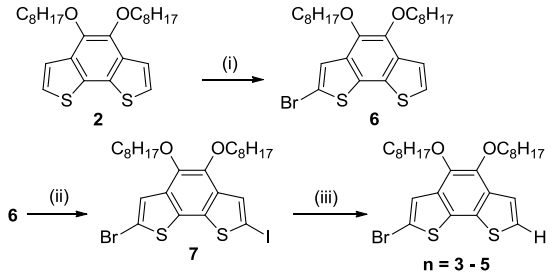
All attempts to prepare selective monochloromagnesio complex from **3** in several temperature conditions were unsuccessful. The best result of the dibromo monomer conversion resulted in an equilibrium mixture of 75% monomagnesio, 5% of dimagnesio and 15% unreacted dibromo monomer (Table 1). The resulting mixture of organomagnesium salt was then tested for KCTP in presence of Ni(dppp)Cl_2. Based on a GPC analysis of the reaction mixture quenched with a few drops of HCl, it appeared that only low molar mass oligomers with a degree of polymerization (DP) of 2-3 were prepared in negligible extent, while the major part of the reaction mixture was constituted by the monomer. This could be attributed to the inefficient GRIM formation which in presence of Ni-catalyst undergoes competitive coupling reactions that inhibit the expected polymerization.

TABLE 1 Outcome of GRIM formation from **3**

Temperature	Time	Products' yield in mixture[a]		
		4	di-GRIM	3
25 °C	0.5 h	50%	10%	40%
25 °C	1-24 h	75%	15%	10%
0 °C	1-4 h	50%	5%	45%

[a] from NMR

In order to selectively prepare the monochloromagnesio complex, we incorporated an iodine atom on the monomer unit, as a iodine atom is more prone to GRIM reaction than Br (Scheme 2). First, compound **6** was synthesized by slow addition of a stoichiometric amount of NBS in a solution of **2** in THF kept at dark and 0 °C. After 4 days, a 50% yield was determined (by ^{1}H NMR analysis of the reaction mixture) alongside **3** (40%) and unreacted **2** (10%). The same reaction conducted in presence of a few drops of HCl resulted in a 70% conversion to **6**. The monobromo derivative **6** was subjected to iodination using iodine and iodobenzene diacetate, resulting in 2-bromo-5-iodo monomer **7** with 86% yield. Compound **7** was successfully converted to its monomagnesium salt (**4**) by addition of a quantitative amount of isopropylmagnesium chloride (complexed with lithium chloride) (^{i}PrMgCl·LiCl) at room temperature within 30 min.



(i) NBS, THF, 48 h, 70%; (ii) I_2, $PhI(OAc)_2$, 24 h, 90%; (iii) 1) ^{i}PrMgCl·LiCl, THF, THF, 2) H^+, 100%

SCHEME 2 Synthesis of the asymmetrically halo-substituted precursor monomer and the actual monomer.

Synthesis of the polymers using Ni(II)-catalysts

The 5-magnesium salt of the **7** in presence of Ni(dppp)Cl_2 underwent KCTP to afford only oligomers of low molar masses (M_n) with the majority of the chloromagnesio salt remaining unconverted (signal at 9.4 min) (Fig. 2a) even after 2 h. This outcome remained unaltered upon extended polymerization reaction time or upon heating up to reflux.

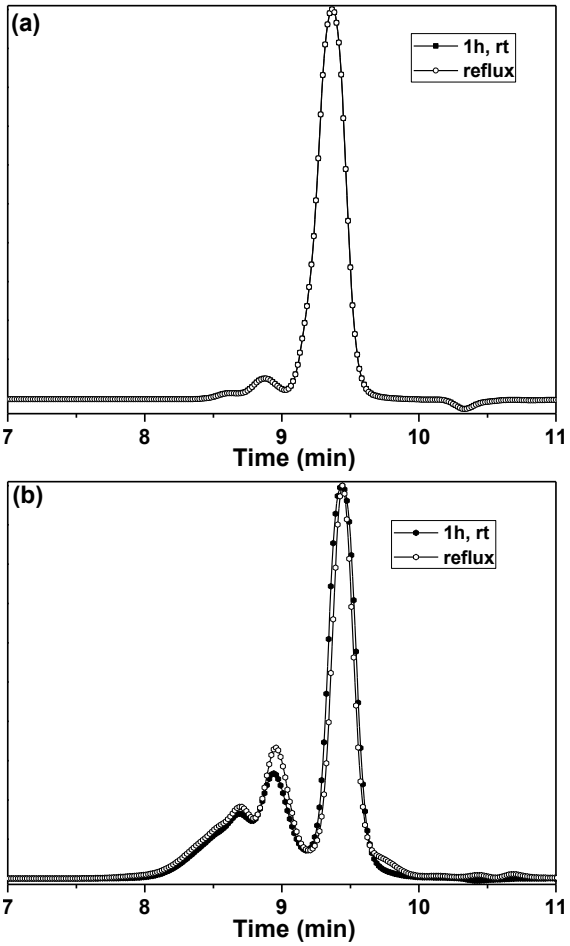
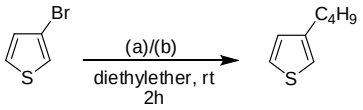


FIGURE 2 GPC analysis of reaction mixture of KCTP using Ni(dppp)Cl_2 (a) and MesAn (b) as catalysts.

Test of poisoning in Ni(dppp)Cl_2

A first explanation for the failure of these polymerizations is the possible occurrence of a very strong complex between Ni(0) and the BDP monomer such as for TT.[25] This poisoning effect of the catalysis prevents it from propagating through the chain. A simple test of a Kumada coupling between 3-bromothiophene and butyl magnesium chloride in absence and presence of **2** rules out such a possibility (Fig. 3). Indeed, under both experimental conditions, the reactions were observed to similarly proceed in terms of reaction time to completion, product and degree of conversion. So the "non-aromatic double bond" in the monomer does not seem to interfere with the catalyst as strongly as TT.[25]



(a) BuMgCl (b) **2** and BuMgCl

FIGURE 3 Kumada cross-coupling of 3-bromothiophene and butylmagnesium chloride in (a) absence and (b) presence of **2**

Ni(II)diimine complex

The above results prompted the introduction of a Ni(II)-diimine catalyst instead of Ni(dppp)Cl_2. Indeed, MesAn (Fig. 4) was shown to allow the polymerization of an electron deficient benzotriazole monomer in a controlled fashion.[30] Poly(thiophene-*b*-benzotriazole) block co-polymer was also successfully prepared with the use of this catalyst.[31] So, Ni(dppp)Cl_2 was replaced by MesAn keeping all other conditions intact. Three reaction temperatures were used, namely room temperature, 60 °C and reflux. The polymerization was monitored during 24 h. The use of MesAn seems to improve the KCTP reaction in terms of monomer consumption, although the major part of the resulting reaction mixture remains constituted by the unreacted monomer. Higher M_n oligomers were observed, without reaching long enough oligomers to consider the global process as a successful polymerization (Fig. 2b). This additional data increases the complexity for understanding KCTP of BDP as polymerization is unsuccessful either under general conditions for electron rich building blocks or electron deficient ones.

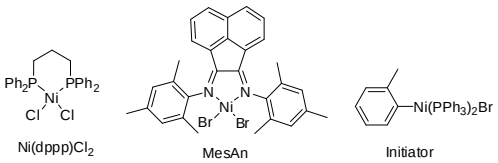
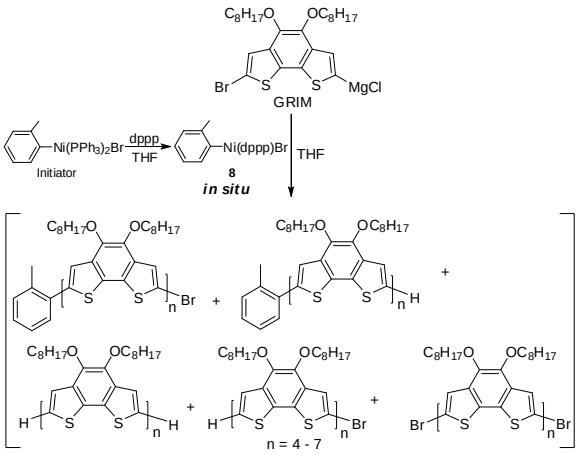


FIGURE 4 The three Ni(II)-catalysts/initiator used.

Synthesis of the polymers using external initiator

All the previous results are gathered in Table 2. In order to get more information on the intrinsic reasons leading to the failure of the polymerization reaction, an external initiator[32-34] was used, since end-group analysis of the resulting polymers/oligomers through MALDI MS is likely to help identifying undesired side-reactions.[35,36] This initiator (Fig. 4) was synthesised by oxidative addition of $Ni(PPh_3)_4$ to *o*-tolyl bromide.[37]



SCHEME 3 Synthesis of the polymer with Ni(II) In/cat system

The polymerization was carried out at room temperature and monitored by GPC (Scheme 3, Fig. 5). After 30 minutes, only residual monomers and oligomers were detected with negligible overtime evolution. The "polymer" was precipitated and purified by Soxhlet extraction using methanol and acetone to remove the residual monomers. Then, MALDI-ToF analysis was performed in order to identify the end-groups. Although the expected signals for the Tol/H polymers were detected, the dominant peak distribution was assigned to polymers containing no *o*-tolyl group (Fig. 6).

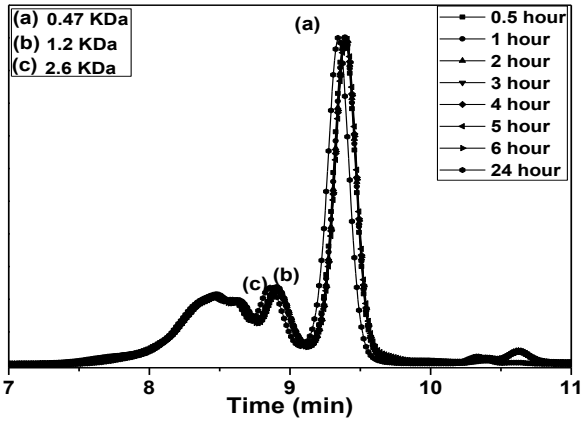


FIGURE 5 GPC spectra of the reaction mixture of polymerization of the GRIM monomer in presence of In/cat. The inset shows the M_n values corresponding to the peaks

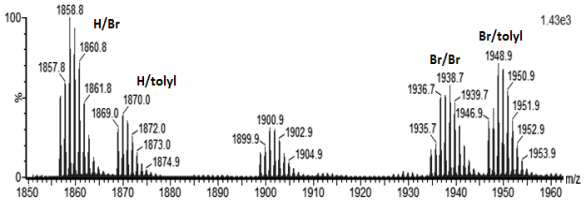


FIGURE 6 MALDI-ToF spectrum of the polymer after Soxhlet extraction.

TABLE 2 Outcome of KCTP from various catalyst or In/cat

Catalyst system	DP
$Ni(dppp)Cl_2$	2-3
MesAn	3-5
In/cat	3-7[a]

[a] After Soxhlet. From GPC and ^1H NMR, it was found impure due to mixture of oligomer with DP of 7 with it (Fig. S2, S2).

So, a side-reaction is responsible for the failure of the KCTP of **BDP-Oct** that is neither associated with too strong catalyst binding (such as in TT), nor the too weak interaction between the catalyst and the monomer (as in electron deficient monomers). In this mechanism, the GRIM monomer underwent KCTP to grow further to form a mixture of oligo-**BDP-Oct** having a chain length of 3-7 and dominated by the oligomer of DP 4. This

particular DP can be concluded from the fact that de dominant series of peaks corresponds to oligomers with DP=4. This can only happen if there is a clear catalyst transfer from the growing chain of the o-tolyl end-capped polymer chain to a new monomer. This is related with the imperfect catalyst association with the conjugated system as recently reported by Nojima *et. al*.[24] This could also be attributed to the intermolecular transfer of Ni(0) from the π-face of the substrate to the C=C of another monomer. It can be speculated that "non-aromatic double bond"present in BDP can fulfill the same role as the double bond, resulting in this transfer reaction. The polymers that were initiated by the external tolyl initiator and of which the catalyst was transferred to a monomer, result in Br/tolyl capped polymers, which are indeed observed. The polymers that were initiated by the transfer of the catalyst to monomer lack a tolyl function; also these are observed.

The polymerization was further monitored by ^{31}P NMR spectroscopy (Fig. 7). This revealed that even after 10 min, the external initiator is fully consumed. The failure of the polymerization can therefore not be attributed to improper initiation.

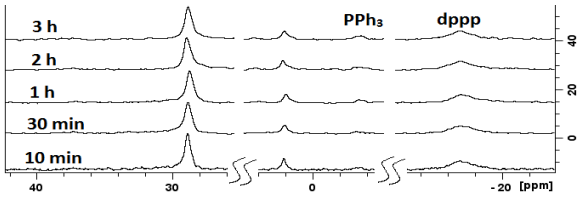


FIGURE 7 *In situ* ^{31}P NMR spectrum of the reaction mixture of KCTP using In/cat monitored during 3 h scale. Spectra were measured in THF and calibrated towards a H_3PO_4 reference.

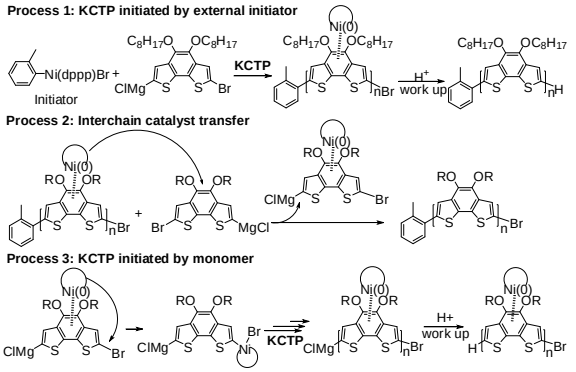


FIGURE 8 Probable competitive reactions for chain propagation and termination through catalyst transfer

From the observed features from GPC (Fig. 2,5), MALDI (Fig. 6) and ^{31}P NMR (Fig. 7), we can propose the reactions that occur during the polymerization (Fig. 8). The first step, the initiator and growth of the polymer (Process 1) happens with excellent conversion as no peak in ^{31}P-NMR for the initiator was observed within 10 min of addition of GRIM to it. However after reaching a DP of 4-5, the Ni(0) species is transferred to a fresh monomer (Process 2) and then oligomers without *o*-tolyl end-group start growing (Process 3). This is similar to the interchain catalyst transfer reported for the Pd(0) species when double bonds are present in the monomer.[24] This process results in the formation of H/Br terminated oligomers of **BDP-Oct**. Finally, the competitive transfer, associated to the catalyst instability, leads to no complete conversion of the GRIM monomer.

CONCLUSIONS

Based on GPC, ^{31}P NMR spectroscopy and MALDI-ToF analyses, it is revealed that the KCTP reaction fails on BDP, whatever the tested catalysts are, because of the occurrence of a competitive transfer reaction of the catalyst from the growing chain to the monomer. Since the isomeric BDT monomer can be polymerized in a controlled polymerization, this cannot be attributed to the presence of specific groups or to the electron efficient or deficient nature of the monomer. Instead, we hypothesize that this is due to the presence of a "non-aromatic

double bond". This result implies that annulated aromatic rings having such "non-aromatic double bond" will probably be very challenging to polymerize in a controlled polymerization that relies on catalyst association.

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GRAPHICAL ABSTRACT

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Detrimental Ni(0) transfer in Kumada catalyst transfer polycondensation of benzo[2,1-*b*:3,4-*b*']dithiophene

An in-depth study of Kumada catalyst transfer polycondensation (KCTP) of a fused monomer unravels that after few initial steps of correct polymerization the Ni(0) species interacts with the "non-aromatic double bond" in the π-system neither very strongly nor too weak to undergo a catalyst transfer to a fresh monomer (which starts polymerizing then individually) thus terminating the correctly initiated polymerization abruptly.